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D E C L A R A T I O N

In the matter of U.S. Patent Appln. Ser. No. 09/374,344 in the name of TOTO LTD.

I, KONNO Akio, of Kyowa Patent and Law Office, 2-~~3~~, Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare and say:

that I am thoroughly conversant with both the Japanese and English languages; and,

that the attached document represents a true English translation of Japanese Patent Application No. 7-99425 filed on March 20, 1995.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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KONNO Akio

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Title of the Invention: A STAIN-RESISTANT FILM, A STAIN-RESISTANT MEMBER FORMED THEREBY, AND METHOD OF MAKING THEREOF

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SPECIFICATION

1. TITIE OF THE INVENTION

A STAIN-RESISTANT FILM, A STAIN-RESISTANT MEMBER FORMED THEREBY, AND METHOD OF MAKING THEREOF

2. CLAIMS

1. A stain-resistant film comprising: a resin, whose surface is subjected to a hydrophilization process, comprised of a photo-resistant component; and a substance having a photocatalytic function.

2. A stain-resistant film according to claim 1, wherein a contact angle with water is less than 70°.

3. A stain-resistant film according to claim 1, wherein said substance having a photocatalytic function is comprised mainly of an inorganic oxide crystalline material.

4. A stain-resistant film according to claim 1, wherein said substance having a photocatalytic function is comprised of an inorganic oxide crystalline material and a metal having an electronic uptake effect.

5. A stain-resistant film wherein, in the stain-resistant film according to claim 1, the ratio by weight of the substance having a photocatalytic function versus the sum of said photo-resistant resin and substance having a photocatalytic function is more than 5% and less than 95%.

6. A stain-resistant film according to claim 1, wherein said photo-resistant resin is a resin such as a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin, that is comprised mainly of a Si-O or Si-N bond.

7. A stain-resistant film according to claim 1, wherein said hydrophilic process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in said photo-resistant resin.

8. A stain-resistant film wherein the stain-resistant film according to claims 1-7 is fixed through a resin binder layer on a substrate surface.

9. A method of making a stain-resistant member, comprising the steps of: applying on a substrate surface a mixture in which a curing agent is added to a photosetting resin or a thermosetting resin; further applying thereon a liquid obtained by adding to the precursor of a substance having a photocatalytic function the photosetting resin having a skeleton comprised of a photo-resistant component or the thermosetting resin, followed by a diluent, and further the curing agent; curing said photosetting resin or thermosetting resin by heat treatment to obtain a intermediate member; and oxidizing or decomposing for hydrophilization a photosetting resin exposedly-formed on the surface of said intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin.

10. A method of making a stain-resistant member according to claim 9, wherein said heat treatment is performed at 100℃ or more and at less than the heat-resistant temperatures of the substrate and thermosetting resin.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a stain-resistant film formed on a substrate used in a water environment, i.e. a bathtub, full-time bath, washbowl, sink, toilet, exterior building material and the surface of part thereof so as to allow them to be utilized preferably.

[0002]

[Prior Art]

Conventionally, stainless metal materials, plastic materials like FRP and ABS, and inorganic materials like enamel, tiles and sanitary ware, have been used in a water environment.

[0003]

However, there is a problem that these materials to which a stained component adheres heavily, involve much cleaning labor. Thus, recently use of water-repellent resins have been suggested to avoid heavy adhesion of a stained component.

[0004]

[Problems to be Solved by the Invention]

However, a water-repellent resin like a fluoro resin is generally soft and is easy to be scratched. There is a disadvantage that, once the surface of it is scratched,

stains deposit outwardly therefrom easily, with strong adhesion. When the part is left for several days, there is a tendency to make the stain adhesion more heavily by bacteria growth.

[0005]

In view of the above facts, an object of the present invention is to offer a stain-resistant film that is rendered resistant to heavy stains, has a sufficient film strength not to be scratched, and avoids bacteria growth.

[0006]

[Means to Solve the Problems]

To solve the above problem, the present invention offers a stain-resistant film comprised of a photo-resistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function.

[0007]

In the preferable embodiment of the present invention, a contact angle with water is less than 70°, more preferably less than 30°.

[0008]

In the preferable embodiment of the present invention, the substance having a photocatalytic function is comprised mainly of an inorganic oxide crystalline material.

[0009]

In the preferable embodiment of the present invention, the substance having a photocatalytic function is comprised of an inorganic oxide crystalline material and a metal having an electronic uptake effect.

[0010]

In the preferable embodiment of the present invention,

the ratio by weight of the substance having a photocatalytic function versus the sum of the photo-resistant resin and substance having a photocatalytic function is more than 5% and less than 95%.

[0011]

In the preferable embodiment of the present invention, the photo-resistant resin is a resin such as a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin, that is comprised mainly of a Si-O or Si-N bond.

[0012]

In the preferable embodiment of the present invention, the hydrophilic process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in the photo-resistant resin.

[0013]

In the preferable embodiment of the present invention, the above stain-resistant film is fixed through a resin binder layer on a substrate surface.

[0014]

A method of making a stain-resistant member of the present invention, is comprised of the steps of: applying on a substrate surface a mixture in which a curing agent is added to a photosetting resin or a thermosetting resin; further applying thereon a liquid obtained by adding to the precursor of a substance having a photocatalytic function the photosetting resin having a skeleton comprised of a photo-resistant component or the thermosetting resin, followed by a diluent, and further the curing agent; curing said photosetting resin or thermosetting resin by heat treatment to obtain a intermediate member; and oxidizing or

decomposing for hydrophilization a photosetting resin exposedly-formed on the surface of the intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin.

[0015]

The above photosetting resin refers to a resin cured by irradiating a light including a UV, to name e.g. a phosphagen resin, epoxy resin and so on.

[0016]

The above thermosetting resin refers to a resin having a property cured by heating, to name a fluororesin, siloxane resin, silane resin, silazane resin, epoxy resin and so on.

[0017]

The above resin having a skeleton comprised of a photo-resistant component, is made of a photo-resistant component in the mainly formed part of a highpolymer chain, to name i.e. a siloxane resin, fluororesin,silane resin, silazane resin and so on.

[0018]

The above precursor of a substance having a photocatalytic function refers to a substance changing into a substance having a photocatalytic function at least after completion of all steps, to name e.g. a sol suspension of a substance having a photocatalytic function.

[0019]

The above hydrophobic surface refers to a surface comprised of a hydrophobic functional group like an alkyl group on a resin surface.

[0020]

The heat treatment of the above making method is

preferably performed at 100℃ or more and at less than the heat-resistant temperatures of the substrate and thermosetting resin.

[0021]

[Effect]

A stain-resistant film is comprised of a photo-resistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function so as to be rendered resistant to heavy fur and to have a sufficient film strength not to be scratched.

[0022]

Being rendered resistant to heavy fur is because the surface of a stain-resistant film is subjected to a hydrophilization process. This is probably because the surface subjected to a hydrophilization process when used in a water environment, makes a contact angle with a large amount of water in surroundings very low, spreading a droplet uniformly in a thin film form to avoid adhesion of an organic component (such as protein and fat) with many hydrophobic parts of main stain components.

[0023]

However, polyamide and polyvinylidene fluoride, a highpolymer hydrophilic that are broadly known in general, are soft and have a weak film strength for film forming. The point can be solved by being rendering only the surface of a resin with a strong film strength hydrophilic.

[0024]

In that event, addition of a substance having a photocatalytic function can first decompose or oxidize an

organic component hydrophobic on the surface of a resin having a strong film strength simply by irradiating a UV. Therefore, a hydrophilization process can easily be realized. Further, a trace of an absorbed component adhered on the surface rendered hydrophilic, based on a photocatalytic function, can decompose such component, maintaining its hydrophilicity as long as the light is irradiated. At this point, a contact angle with water is about 5° at production, but is different from that of glass whose surface is rendered hydrophobic gradually with use. Second, active oxygen generated from the substance having a photocatalytic function can increase deodorizing and antibacterial effects.

[0025]

Being rendered hydrophilic to a degree that a contact angle with water is less than 70°, more preferably less than 30°, will be resistant to heavy stains.

[0026]

It is understood that the substance having a photocatalytic function is comprised mainly of an inorganic oxide crystalline material so that the surface is rendered resistant to alkali or alkaline earth metal by adding an inorganic oxide crystalline material. In other words, adhesion of alkali or alkaline earth metal on the surface of a substrate, may cause a stain component like fat to react to adhesive alkaline earth metal, to adhere an insoluble soap stain on the surface; but it is thought that this can be prevented effectively.

[0027]

The substance having a photocatalytic function is

comprised of an inorganic oxide crystalline material and a metal having an electronic uptake effect so as to be resistant to heavy stains. This is because addition of the metal having an electronic uptake effect allows an electron of electrons and holes generated by the substance having a photocatalytic function to be trapped by the metal, decreasing the diminished probability of the holes by reunion with the electrons; whereby the probability that the holes react to oxygen diffused from the air to generate active oxygen is increased, improving the probability that an organic component hydrophobic is decomposed or oxidized at UV irradiation. Further, increasing the probability of generating active oxygen improves deodorizing and antibacterial effects.

[0028]

The ratio by volume of the substance having a photocatalytic function versus the sum of the photo-resistant resin and the substance having a photocatalytic function, is more than 5% and less than 95%; an organic component hydrophobic on the surface of a resin having a particularly sufficient film strength and having a strong film strength, can be decomposed or oxidized simply by irradiating a UV for a short time. Therefore, a hydrophilization process can easily be realized. Furthermore, active oxygen generated from the substance having a photocatalytic function can improve deodorizing and antibacterial effects. In other words, the ratio by volume of 5% or less cannot decompose or oxidize the organic component hydrophobic for a short time, while that of 95% or more cannot realize a sufficient film strength.

[0029]

The photo-resistant resin is a resin such as a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin, that is comprised mainly of a Si-O or Si-N bond; preferably the Si-O or Si-N bond has hydrophilicity and has the most excellent photo resistance in resins.

[0030]

The hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a photo-resistant resin so as to make easily a stain-resistant film having a sufficient film strength.

[0031]

The above stain-resistant film is fixed through a resin binder layer on a substrate surface so as to make the film strength stronger.

[0032]

The stain-resistant member is made by the steps of: applying on a substrate surface a mixture in which a curing agent is added to a photosetting resin or a thermosetting resin; further applying thereon a liquid obtained by adding to the precursor of a substance having a photocatalytic function the photosetting resin or the thermosetting resin, followed by a diluent, and further the curing agent; curing said photosetting resin or thermosetting resin by heat treatment to obtain a intermediate member; and oxidizing or decomposing for hydrophilization a photosetting resin exposedly-formed on the surface of the intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin, so that a stain-resistant

member having a surface rendered hydrophilic can easily be obtained.

[0033]

The heat treatment of the above making method is performed at 100℃ or more and at less than the heat-resistant temperatures of the substrate and thermosetting resin, whereby a particle comprised of the substance having a photocatalytic function has a specific gravity higher than that of the thermosetting resin, and the particle comprised of the substance having a photocatalytic function is concentrated on the upper part, so as to shorten the time for decomposing or oxidizing for hydrophilization a photosetting resin exposedly-formed on the surface of the intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin.

[0034]

[Embodiment]

The concrete embodiments of the present invention are explained based on the drawings. Fig. 1 is a diagram showing an embodiment of the present invention, wherein a film comprised of a photo-resistant resin rendered hydrophilic and a substance having a photocatalytic function, is formed through a resin binder layer on a substrate surface.

[0035]

Fig. 2 is a diagram showing another embodiment of the present invention, wherein a film comprised of a photo-resistant resin rendered hydrophilic,a substance having a photocatalytic function, and a metal having an electronic uptake effect, is formed through a resin binder layer on a substrate surface.

[0036]

Any material for the substrate such as ceramic, pottery material, metal, glass, plastic, decorative plywood, calcium silicate, mortar or composite thereof, may basically be used.

[0037]

Any shape of the substrate may be used; for example, a simple shape such as a tile, wall material, board like floor material, spherical, cylindrical, cylindroid, bar, prism and hollow prism; a complex shape such as sanitary ware, washstand, bathtub, sink and accessary thereof, may be included.

[0038]

The photo-resistant resin refers to a good photo-resistant resin, such as a silicon resin, siloxane resin, fluoro resin, and polysilazane resin.

[0039]

The substance having a photocatalytic function refers to a substance that generates an electron and hole by irradiating a light at below a constant wavelength, producing active oxygen. Such substances are titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, dibismuth trioxide, and tin oxide. These substances may be used alone or used together.

[0040]

The inorganic oxide crystalline material refers to an inorganic oxide crystalline material that is crystallized above a degree that the peak is observed for powder X-ray diffraction.

[0041]

The metal having an electronic uptake effect refers to a metal such as Pt, Pd, Au, Ag, Cu, Ni, Fe, Co and Zn, that has a low ionization tendency and is easily self-reduced. A multiple kind metals may be used together.

[0042]

The resin binder layer may be any of a thermosetting resin, photosetting resin or thermal plasticity resin; especially the thermosetting resin or photosetting resin is only applied on the layer to be heat-treated so as to form the layer relatively smooth. Also, selection and use of said resin having a favorable thermal expansion coefficient depending on the kind of a substrate, are preferable because of crack resistance. Further, a colored resin for the layer may be used to thereby be provided with a design.

[0043]

A method of making a stain-resistance member shown in Figs. 1 and 2 is summarized. First, a method of making a stain-resistant member wherein a film comprised of a photo-resistant resin rendered hydrophilic and a substance having a photocatalytic function is formed through a resin binder layer on a substrate surface as shown in Fig. 1, is explained by taking an example in the case where the substrate is an aluminum substrate; the resin binder layer is a thermosetting resin comprised mainly of a siloxane resin; and the substance having a photocatalytic function is anatase-form titanium oxide.

[0044]

In this case, a stain-resistant member can basically be made by the steps of: applying on an aluminum substrate

surface a mixture in which a curing agent is added to a siloxane resin; further applying thereon a liquid obtained by adding to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent,and further the curing agent; curing the siloxane resin by heat treatment to obtain an intermediate member; and oxidizing (Formula 2) or decomposing (Formula 3) for hydrophilization R part (Formula 1) comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of said intermediate member by UV light irradiation.

[0045]

[Formula 1]

[0046]

[Formula 2]

[0047]

[Formula 3]

[0048]

Basically, any method may be used to apply on an aluminum substrate surface a mixture wherein a curing agent is added to a siloxane resin, but spray coating and roll coating are relatively easy.

[0049]

After applying on an aluminum substrate surface a mixture wherein a curing agent is added to a siloxane resin, drying may be inserted before further applying thereon a liquid obtained by adding to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent,and

further the curing agent. This makes the substrate surface smooth at applying said liquid, applying the liquid more uniformly.

[0050]

The anatase-form titanium oxide sol dispersed sufficiently in a suspension is preferable. For that reason, the anatase-form titanium oxide with a PH 6.5 electric point, is dispersed by under acidic or alkaline conditions. In this case, to improve its dispersion, a finishing activator, a dispersing agent (deflocculant), or a finishing agent, may be added. Any solvent to disperse the anatase-form titanium oxide sol may basically be used. In general, water or ethanol is often used.

[0051]

The siloxane resin is added to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent so as to lower the viscosity of the liquid to easily be applied on the substrate. Any diluent to reach this purpose may basically be used. For example, ethanol, propanol or water can preferably be used.

[0052]

The liquid is made in the order of adding to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent, further the curing agent, whereby the liquid to be applied on the substrate can be generated without agglomerating the suspension.

[0053]

Any method of applying the liquid on the substrate may basically be used,but spray coating and roll coating are relatively easy.

[0054]

The heat treatment may be performed at low temperatures of less than 100℃ for a long time, but may preferably be performed at 100℃ or more and at less than the heat resistant temperatures of the substrate and thermosetting resin for a short time. In general, a particle comprised of a substance having a photocatalytic function has a specific gravity greater than that of a thermosetting resin. The heat treatment at 100℃ or more and at less than heat resistant temperatures of the substrate and thermosetting resin is preferable, because the particle comprised of a substance having a photocatalytic function is concentrated on the upper part, so as to shorten the time for decomposing or oxidizing for hydrophilization R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation.

[0055]

The Auger electron spectroscopy results of the element analysis in the cross-sectional direction of the above intermediate member, are shown in Fig. 3 (a) - (c). Nitric acid was used for suspending an anatase-form titanium oxide sol,and a heat treatment was performed at 150℃.

[0056]

In Fig. 3 (a), Si, C, N and O can be observed on a sample outermost surface, but Ti not. However, as shown in Fig. 3 (b), Ti as well as Si, C, N and O can be observed at 20 nm under the sample outermost surface. As shown in Fig. 3 (c), at 200 nm under the surface is a layer comprised only of a siloxane resin, and only Si, C and O that are

components thereof can be observed. Thus, it is considered that one layer comprised only of a siloxane resin is formed on the sample outermost surface of the intermediate member.

[0057]

R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation, is decomposed or oxidized for hydrophilization by the action of active oxygen generated from anatase-form titanium oxide at about 20 nm under the surface.

[0058]

The UV light refers to a light including a light with a short wavelength to a degree of energy enough to excite an electron from a valence electron band to a conductive band in a substance having a photocatalytic function, so that a light including a light of less than 400 nm is irradiated for anatase-form titanium oxide.

[0059]

Next, a method of making a stain-resistant member wherein a film comprised of a photo-resistant resin rendered hydrophilic, a substance having a photocatalytic function, and a metal having an electron uptake effect is formed through a resin binder layer on a substrate surface as shown in Fig. 2, is explained by taking an example in the case where the substrate is an aluminum substrate; the resin binder layer is a thermosetting resin comprised mainly of a siloxane resin; the substance having a photocatalytic function is anatase-form titanium oxide; and the metal having an electron uptake effect is copper.

[0060]

In this case, a stain-resistant member can basically be made by the steps of: applying on an aluminum substrate surface a mixture in which a curing agent is added to a siloxane resin; further applying thereon a liquid obtained by mixing an anatase-form titanium oxide sol suspension with a solution including a copper ion, and adding to the mixture a siloxane resin, followed by a diluent, and further the curing agent; curing the siloxane resin by heat treatment to obtain an intermediate member; and decomposing or oxidizing for hydrophilization R part (Fig. 3) comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of said intermediate surface by UV light irradiation.

[0061]

A soluble, copper compound solution such as cupric acetate and cupric sulfate can preferably be used for the solution including a copper ion. In the case of a metal having an electron uptake effect, other than copper, a soluble solution such as silver nitrate, silver sulfate, silver lactate, and silver acetate is preferable for making a mixing treatment easy. Also, a solvent such as water, ethanol and propanol can be used for the solution including a copper ion, but the same kind of anatase-form titanium oxide sol suspension is preferable, where possible.

[0062]

In mixing an anatase-form titanium oxide sol suspension with a solution including a copper ion, the PH of the solution including a cooper ion should be adjusted almost equal to the PH of the anatase-form titanium oxide

suspension; because a change in the PH of the anatase-form titanium oxide sol suspension is small, damaging remarkably no dispersion of the anatase-form titanium oxide sol in the suspension.

[0063]

After mixing an anatase-form titanium oxide sol suspension with a solution including a copper ion, a UV light may be irradiated on this solution. This allows copper to be photo-reducibly fixed on the anatase-form titanium oxide particle, promoting a hydrophilization process at a smaller amount of copper.

[0064]

The effect of the above embodiment is explained below based on concrete evaluating experiments.

(Evaluating experiment 1)

First, a variety of resins were used to check the relation between a contact angle with water and stain adhesion. The contact angle with water was measured with a contact angle measuring instrument. For the stain adhesion, as shown in Fig. 4, a sample 6 was immersed in an artificial bathtub 7 (warm water mixed with human being's dirt, lard, and soap) for 3 hours. the specific glossinesses around a level surface before and after immersion were obtained for an evaluating index.

[0065]

The specific glossiness refers to a immersion glossiness when the initial glossiness before immersion is 1.

[0066]

The results are shown in Fig. 5. In the diagram, the

specific glossiness was the lowest at a contact angle with water of around 70° and was easy to adhere stains. The specific glossiness was improved more in a decrease in the contact angle with water than in an increase in the contact angle, and was almost unchanged at less than 30°.

According to the above, it was evident that a contact angle with water of less than 70°, more preferably at less than 30° makes stain resistance.

[0067]

(Evaluating experiment 2)

About 3 μm of a mixture in which a curing agent was added to the siloxane resin, was applied on a 10 cm square aluminum substrate, and then was heat-treated at 150℃ to obtain an intermediate member C. A BLB lamp was irradiated on this intermediate member for 5 days to obtain a comparing sample A.

[0068]

A liquid obtained by adding the siloxane resin to a liquid in which a nitrate-dispersed liquid of a titanium oxide sol with a 0.01 μm average particle diameter was mixed with a 3% copper acetate water solution by weight (the ratio by weight of the titanium oxide versus siloxane resin is 1 : 1), and by diluting with propanol to further add a curing agent, was applied on the surface of the above intermediate member C, and then was heat-treated at 150℃ to obtain an intermediate member. The BLB lamp was irradiated on this intermediate member D for 5 days to obtain an embodiment sample B.

[0069]

The contact angles with water for these samples A and

B, and intermediate members C and D, were measured with a contact angle measuring instrument. The results are shown in Table 1. According to the table, the contact angle with water was at a high 70° in the comparing sample A, while the angle was a low 40° in the intermediate member D with which titanium oxide was mixed. Further, the embodiment sample B subjected to a hydrophilization process by irradiating a BLB lamp, was sufficiently rendered hydrophilic with the angle of 3°.

[0070]

Table 1

[0071]

The stain adhesion for the embodiment sample B obtained here, was tested with the same method as the evaluating experiment 1. As a result, a change in the specific glossiness was less than 1%, showing a favorable result.

[0072]

Further, the antibacterial properties of the samples A and B, and intermediate members C and D, were evaluated. They were evaluated with a colon bacillus (Escherichia coli W3110 stock). Glass plates (100 x 100) on which an bacterial liquid of 0.15 ml (10000 - 50000CFU) was dropped, were contacted on the outermost surfaces of the above samples and intermediate members sterilized with 70% ethanol beforehand, and then were subjected to irradiation of a white light (3500 lux) for 30 minutes. The bacterial liquid thereon was wiped away with sterilized gauze to be recovered to a physiological salt water of 10 ml. Then, the survival rate of the bacteria was found for an evaluating

index. The evaluating indexes are shown below.

+++: The survival rate of the colon bacillus is less than 10%.

++ : The survival rate of the colon bacillus is 10% or more and less than 30%.

+ : The survival rate of the colon bacillus is 30% or more and less than70%.

- : The survival rate of the colon bacillus is 70% or more.

As a result, the intermediate member C and the comparing sample A showed -, while the intermediate member D and the embodiment sample B showed a favorable result of +++.

[0073]

Further, the deodorizing properties of the samples A and B, and the intermediate members C and D, were evaluated. They were evaluated by measuring R30 (L). The R30 (L) refers to the removed rate of an odor component after light irradiation. Concretely, the rate can be obtained by placing 8 cm away from a light source (BLB lamp 4W) a surface in a 11L glass vessel on which a stain-resistant film of each of the samples or members was formed, by filling methylmercaptan gas into the vessel such that the gas has an initial concentration of 3 ppm, and measuring a change in the concentration for 30-minute light irradiation.

[0074]

The R30 (L) value was less than 10% in the intermediate member C and the comparing sample A; while the value was 80% or more in both of the intermediate member D and the embodiment sample B, showing a favorable result.

[0075]

(Evaluating experiment 3)

About 3 μm of a mixture in which a curing agent was added to the siloxane resin, was applied on a 10-cm square aluminum substrate, and then was heat-treated at 150℃ to obtain an intermediate member. A liquid obtained by adding the siloxane resin with the ratio by weight of the titanium oxide versus the siloxane resin changed, to a liquid in which a nitrate-dispersed liquid of a titanium oxide sol with a 0.01 μm average particle diameter was mixed with a 3% copper acetate water solution by weight, and by diluting with propanol to further add a curing agent, was applied on the surface of this intermediate member, and then was heat-treated at 150℃ to obtain an intermediate member. The BLB lamp was irradiated on this intermediate member D for 5 days to obtain an embodiment sample. Contact angle measurement and a wear-resistant test were conducted for the obtained sample.

[0076]

In the wear-resistant test, slided wearing with a plastic eraser was performed, and changes in an appearance were compared for evaluation. The evaluating references are shown below.

◎: No change in 40 slidings.

○: 10 or more and less than 40 slidings caused a stain-resistant film to be scratched and peeled off.

△: 5 or more and less than 10 slidings caused a stain-resistant film to be scratched and peeled off.

×: Less than 5 slidings caused a stain-resistant film to be scratched and peeled off. The results are shown Fig. 6.

According to the diagram, when the weight of the titanium oxide in the stain-resistant film is less than 95%, preferably 90% or less, the wear resistance shows a favorable result of ◎. In addition, when the weight of titanium oxide in the stain-resistant film exceeds 5%, a contact angle is less than 30°, delivering a favorable stain resistance.

[0077]

[Effect of the Invention]

A stain-resistant film is comprised of a photo-resistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function, so as to be resistant to heavy stains, to have a sufficient film strength not to be scratched, and to avoid bacterial growth.

[Brief Description of the Drawings]

Fig. 1

It is a conceptual diagram showing one embodiment of the present invention.

Fig. 2

It is a conceptual diagram showing another embodiment of the present invention.

Fig. 3

It is an Auger electron spectroscopy profile diagram of an intermediate member produced in the producing step of a stain-resistant member according to the present invention; (a) is a sample outermost surface, (b) is at 20 nm under the

sample outermost surface, and (c) is at 200 nm under the sample outermost surface.

Fig. 4

It is a diagram of an apparatus showing a method of evaluating stain resistance.

Fig. 5

It is a diagram showing the relation between a contact angle with water and stain adhesion.

Fig. 6

It is a diagram showing the relation between the weight of titanium oxide, wear resistance and a contact angle in a stain-resistant film.

[Explanation of the Reference Numerals]

1 .... Substrate

2 .... Binder layer

3 .... Photo-resistant resin

4 .... Photocatalytic particle

5 .... Metal particle

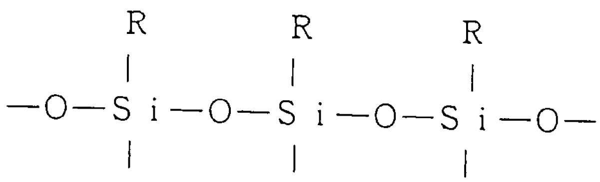
6 .... Sample

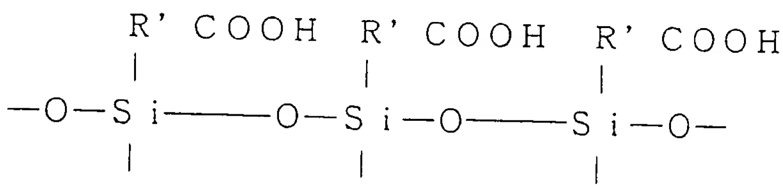
7 .... Artificial bathtub water

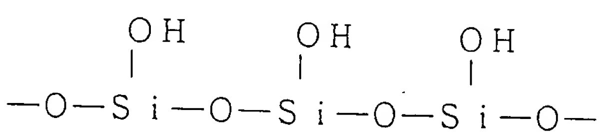
8 .... Dirt

Table 1

Sample	Intermediate member C	Comparing sample A	Intermediate member D	Embodiment sample B
Contact angle (°)	70	70	40	30







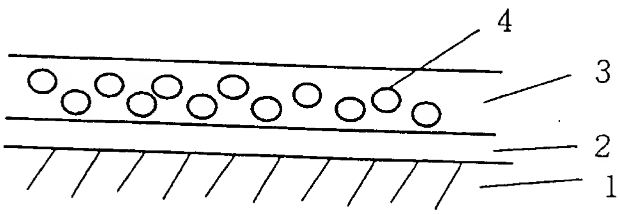


Fig. 1

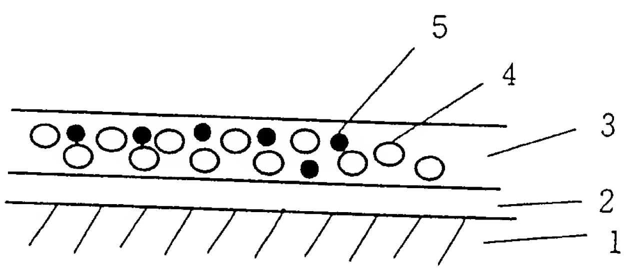


Fig. 2

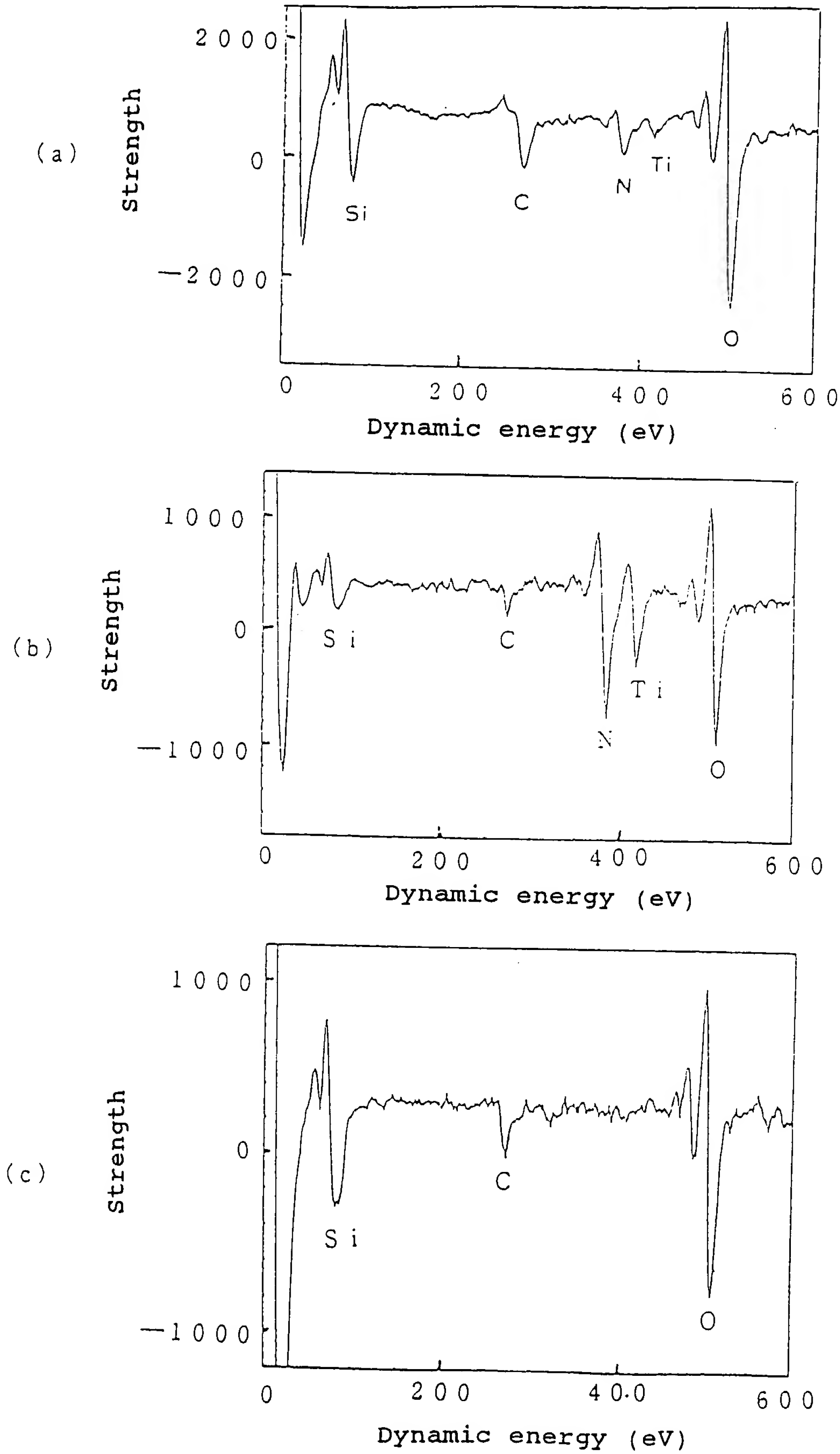

(a)
Strength
2000
0
−2000
Si
C
N
Ti
O
0
200
400
600
Dynamic energy (eV)
(b)
Strength
1000
0
−1000
Si
C
N
Ti
O
0
200
400
600
Dynamic energy (eV)
(c)
Strength
1000
0
−1000
Si
C
O
0
200
400
600
Dynamic energy (eV)

Fig. 3

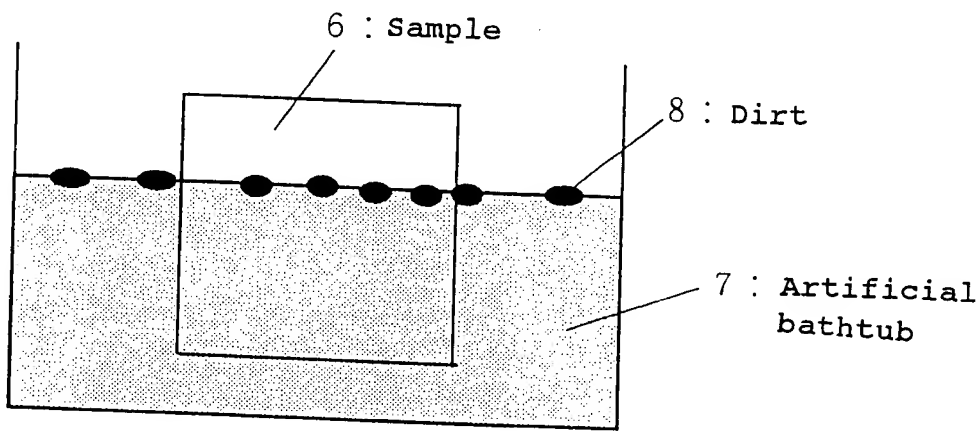

6 : Sample
8 : Dirt
7 : Artificial bathtub

Fig. 4

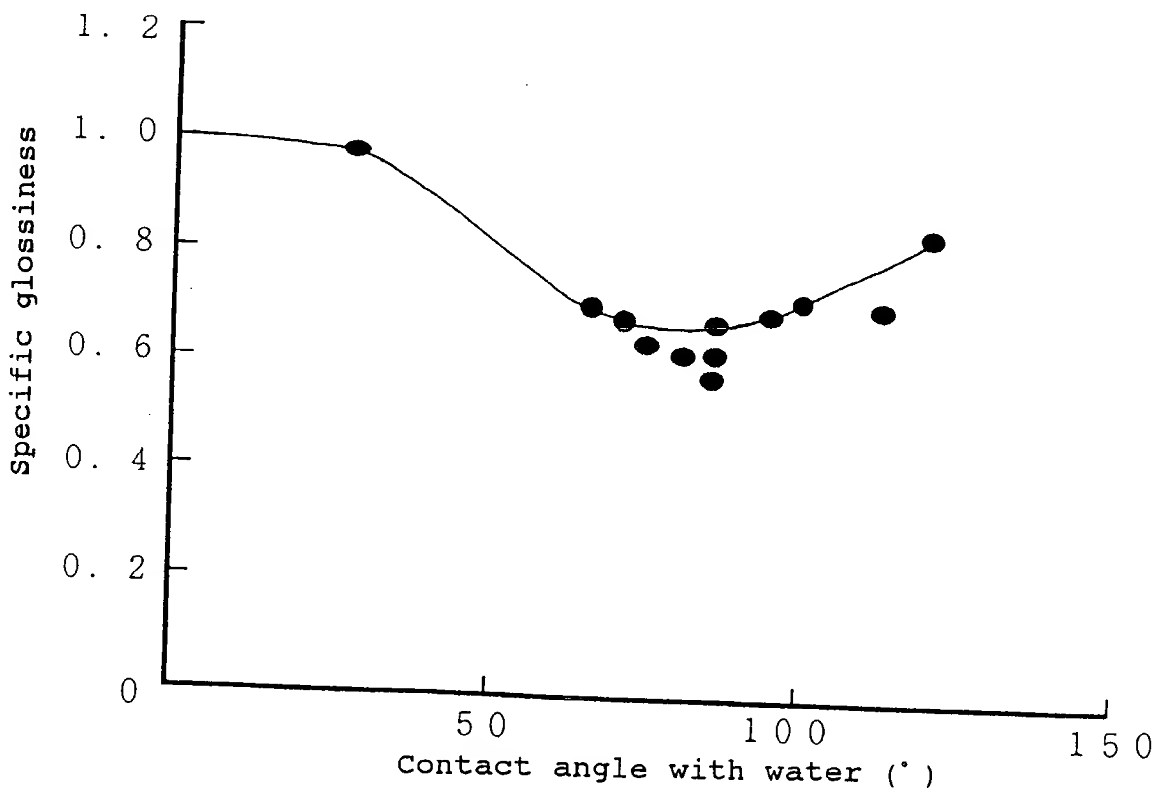

1. 2
1. 0
0. 8
0. 6
0. 4
0. 2
0
Specific glossiness
5 0
1 0 0
1 5 0
Contact angle with water (°)

Fig. 5

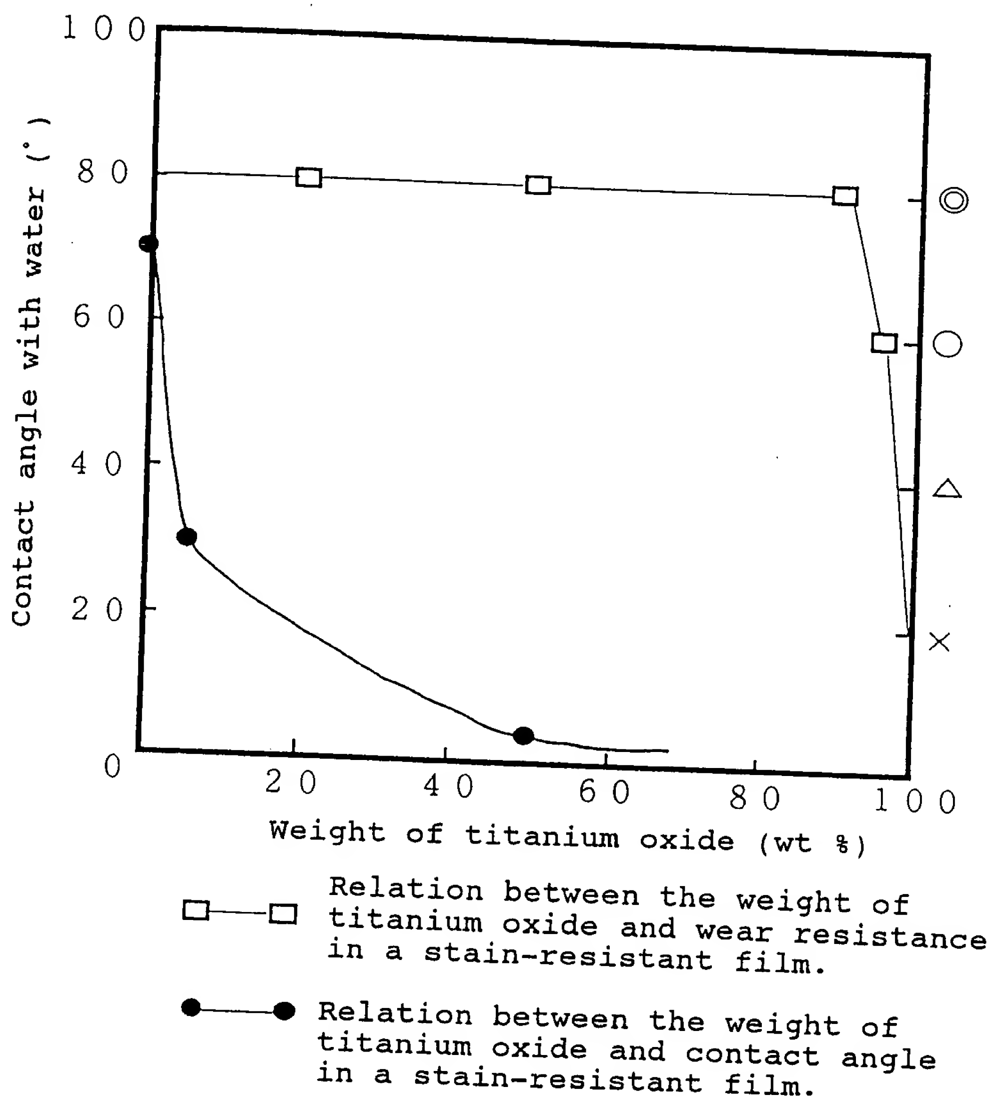

100
80
60
40
20
0
20
40
60
80
100
Contact angle with water (°)
Weight of titanium oxide (wt %)
◎
○
△
×
Relation between the weight of titanium oxide and wear resistance in a stain-resistant film.
Relation between the weight of titanium oxide and contact angle in a stain-resistant film.

Fig. 6

ABSTRACT

[Objects]

It is an object of the present invention is to offer a stain-resistant film allowed to be resistant to heavy stains, to have a sufficient film strength not to be scratched, and to avoid bacterial growth.

[Constitution]

A stain-resistant film comprised of a photo-resistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function.

[Selected Figure]

Fig. 1